INVESTIGATION OF THE CATALYTIC INTERACTION OF HYDROGEN CHLORIDE AND METHANOL.
PART II: KINETICS OF DEHYDRATION OF METHANOL AND HYDROCHLORINATION OF DIMETHYL ETHER ON CATALYSTS USED FOR VAPOR-PHASE SYNTHESIS OF METHYL CHLORIDE

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ABSTRACT. The kinetics of methanol dehydration and dimethyl
ether hydrochlorination in the catalytic vapor-phase synthesis
of chloromethane for organosilicon polymers and butyl rubber
are discussed, with reaction formulas for various catalysts
and second-order equations for the rate of reaction. The rate
of reaction of dimethyl ether with hydrogen chloride is pro-
portional to the first power of the ether and HCl concentration,
with the kinetics described by $w = k \cdot p_{HCl} \cdot p_{(CH_3)_2O} \cdot$ Zinc
chloride was found to be a more selective catalyst for chloro-
methane synthesis than alumina.

Previously, we studied (Ref.1) the kinetics of the vapor-phase catalytic
synthesis of chloromethane from methanol and hydrogen chloride:

(1)

The rate of reaction (1) is described by a second-order equation. Studies of
the activities of a large number of catalysts by the gradient-free method have
shown the most effective to be $ZnCl_2$ applied to Al_2O_3, and Al_2O_3 itself.

All catalysts for methyl chloride synthesis – chlorides of various metals
and alumina – promote to some extent the formation of dimethyl ether as a by-
product:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O. \quad (2)$$

This process takes place at the highest velocity on alumina which catalyzes
the dehydration of alcohols and is retarded when zinc chloride or chlorides of
other metals are applied to its surface.

Dimethyl ether (Ref.2) reacts with hydrogen chloride on these catalysts:

$$(CH_3)_2O + 2HCl \rightarrow 2CH_3Cl + H_2O. \quad (3)$$

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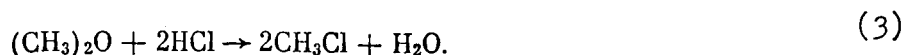
* Numbers in the margin indicate pagination in the foreign text.

Obviously the overall rate of formation of dimethyl ether equals the difference between the rates of reactions (2) and (3).

Dimethyl ether is a harmful impurity in the production of organosilicon polymers and butyl rubber, which are the principal consumers of methyl chloride. The methods of physical or chemical purification ordinarily used involve considerable complications in the production process.

The kinetics of the side reactions in the synthesis of methyl chloride are therefore of considerable interest.

The study of the kinetics of reactions (2) and (3) is also of independent interest, since there are no data in the literature on this subject. The reaction (3) is of practical interest as well, as one of the possible ways of utilizing dimethyl ether, which is a byproduct of a number of industrial processes.

1. Experimental Part

The kinetics of reactions (2) and (3) were studied separately.

The experiments were run on catalysts of 60 mass% $ZnCl_2/Al_2O_3$ and Al_2O_3. The kinetics of the reaction (3) was also studied on a catalyst of 20 mass% $ZnCl_2/AP-3$.

The equipment for studying the kinetics of reaction (2) consisted of a methanol metering device and evaporator, a gradientless reactor, cooler and receiver of the water-methanol condensate, and cold traps for freezing out the dimethyl ether, with the dimethyl ether dissolved in the condensate being evaporated off after the experiment.

$CH_3OH +$

The apparatus used in studying the kinetics of the reaction (3) has been described earlier (Ref.1). The dimethyl ether was synthesized by treating "C.P." methanol with "C.P." sulfuric acid (Ref.3), dried over calcium chloride, and introduced into the system through a flow meter.

The mixture of dimethyl ether and methyl chloride from the freeze trap was analyzed chromatographically. The kinetic measurements were performed under conditions free of diffusional lag.

The experimental method is described in greater detail elsewhere (Ref.1).

a) Kinetics of Dehydration of Methanol

It is well known that reaction (2) is reversible.

The kinetic measurements were made far from the state of equilibrium, permitting a sufficiently accurate interpretation of the observed rate of formation of dimethyl ether as representing the rate of forward reaction. Since the kinetics of reactions (1) and (3) were studied on catalysts whose surface had first been saturated with HCl, special experiments were carried out which showed

that this treatment of the catalyst had no effect on the rate of the reaction (2).

The kinetics was studied by varying the volume rate of methanol feed. In some experiments the gas mixture was diluted with nitrogen.

TABLE 1

DEPENDENCE OF THE RATE OF REACTION (2) ON THE PARTIAL
PRESSURES OF THE COMPONENTS AND ON THE TEMPERATURE

t, °C	Volume Feed Rate ltr/ltr·cat·hr	Stationary Partial Pressures, atm			w, ltr(CH_3)$_2$O/ ltr·cat·hr	10^{-3} $w/p_{CH_3OH}^2$ ltr·atm^{-2}/ltr·cat·hr
		CH_3OH	$(CH_3)_2O$	H_2O		
195	140	0.802	0.099	0.099	29.6	0.461
195	290	0.895	0.052	0.053	45.4	0.567
195	1500	0.97	0.015	0.015	46.4	0.493
225	140	0.55	0.225	0.225	63.6	2.10
225	290	0.665	0.167	0.168	96.2	2.17
225	1860	0.923	0.038	0.039	146	1.71
285	520	0.352	0.324	0.324	335	27.0
285	930	0.514	0.167	0.167	640	24.2
285	3320	0.686	0.157	0.157	1120	24.0
285	3320	0.679	0.160	0.161	1130	24.6
285	3640	0.604	0.105	0.291	767	21.3
285	5550	0.764	0.118	0.118	1380	23.8

Table 1 gives the results of the kinetic measurements on an Al_2O_3 catalyst (195 - 285°C). Figures 1 and 2 give the data for $ZnCl_2/Al_2O_3$ (305 - 365°C) in graphical form.

Calculations showed that the kinetics of the reaction (2) on these catalysts is described by the equation

$$w = k \cdot p^2_{CH_3OH}.$$ (4)

Figure 1 shows that the experimental data are in satisfactory agreement <u>/3057</u> with eq.(4). The constants of the Arrhenius equation for these catalysts have the values:

$$B = 2.4 \cdot 10^8 \quad E = 21800 \text{ kcal/mole} \quad (Al_2O_3)$$
$$B = 8.9 \cdot 10^{18} \quad E = 45700 \text{ kcal/mole} \quad (ZnCl_2).$$

Thus, when the alumina surface is coated with zinc chloride, the rate of methanol dehydration declines sharply.

It should be noted that eq.(4) remained valid when the reaction mixture was diluted with an excess of methyl chloride. Thus, on these catalysts, methanol does not react with methyl chloride to form dimethyl ether.
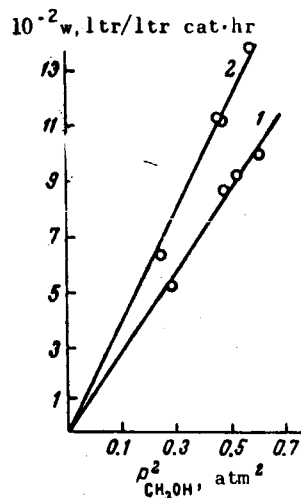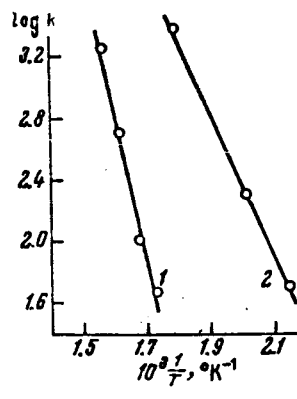
Fig.1   Fig.2

Fig.1 Rate of Reaction (2) vs. Methanol Partial Pressure.
1 - $ZnCl_2/Al_2O_3$ catalyst (365°C); 2 - Al_2O_3 catalyst (285°C).
Fig.2 Temperature Dependence of log k; Reaction (2).
      1 - $ZnCl_2/Al_2O_3$ catalyst; 2 - Al_2O_3 catalyst.

b) Study of the Kinetics of Reaction of Hydrochlorination
   of Dimethyl Ether

The mechanism of the action of the catalysts on the reaction between dimethyl ether and HCl apparently, like reaction (1), is due to aprotonic catalysis. This mechanism has already been discussed by us (Ref.1). In our opinion, the activity of the catalysts in these reactions is largely connected with their acceptor property. The participation of HCl in the nucleophilic attack probably requires its adsorption on the surface, as suggested by the considerable deactivation of the catalyst after its preliminary saturation with dimethyl ether. The activity series of the catalysts of reactions (1) and (3) coincide. The difference between these two reactions consists in the lower reactivity of dimethyl ether.

The assumption is justified that reaction (3) is not the result of a trimolecular collision but proceeds through the successive-parallel stages:

$$CH_3 - O - CH_3 + HCl \xrightarrow{k_3} CH_3OH + CH_3Cl,$$
$$CH_3OH + HCl \xrightarrow{k_1} CH_3Cl + H_2O,$$
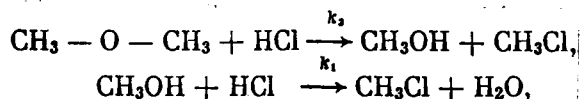
k_1 and k_3 being the rate constants of the respective stages.

In view of the lower reactivity of dimethyl ether, one would expect the /3058 rate-determining stage to be its hydrochlorination ($k_3 < k_1$). In that case the rate of reaction (3) should be proportional to the first power of the concentrations of ether and HCl.

The experimental data fully confirm these assumptions. The results of the

kinetic measurements on Al_2O_3 catalysts (215 - 305°C) are presented in Table 2 and Figs.3 - 4, and on the other catalysts (135 - 225°C) only graphically.

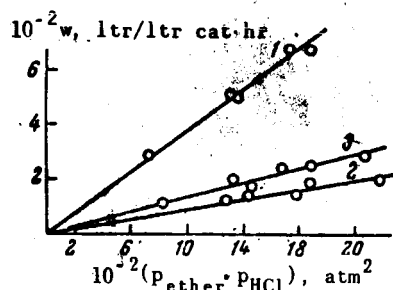Fig.3   Fig.4

Fig.3 Rate of Reaction (3) vs. Product of Partial Pressures
of Dimethyl Ether and HCl.
1 - $ZnCl_2/Al_2O_3$ catalyst (135°C); 2 - Al_2O_3 catalyst (215°C);
3 - $ZnCl_2/AP$-3 catalyst (140°C).
Fig.4 Temperature Dependence of log k; Reaction (3).
1 - $ZnCl_2/Al_2O_3$ catalyst; 2 - Al_2O_3 catalyst; 3 - $ZnCl_2/AP$-3
catalyst.
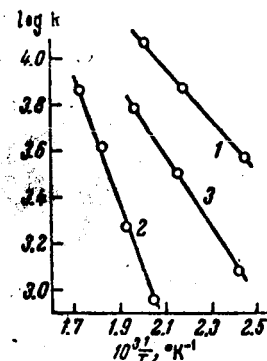
TABLE 2

DEPENDENCE OF THE RATE OF REACTION (3) ON THE PARTIAL
PRESSURES OF THE COMPONENTS AND ON THE TEMPERATURE

t, °C	Volume Feed Rate ltr/ltr·cat·hr	Stationary Partial Pressures, atm				w, CH_3Cl ltr/ltr·cat·hr	10^{-3} $w/P_{HCl}P_{(CH_3)_2O}$ ltr/ltr cat·hr·atm²
		$(CH_3)_2O$	HCl	H_2O	CH_3Cl		
215	4890	0.695	0.256	0.016	0.033	141	0.791
215	4850	0.456	0.480	0.021	0.043	172	0.786
215	4780	0.300	0.627	0.024	0.049	191	1.01
215	14900	0.203	0.631	0.156	0.010	123	0.96
215	4700	0.180	0.766	0.018	0.036	141	1.02
245	4720	0.701	0.191	0.036	0.072	281	2.10
245	4690	0.452	0.424	0.041	0.083	322	1.68
245	6700	0.169	0.482	0.228	0.121	136	1.67
245	4670	0.166	0.733	0.034	0.067	158	2.16
245	9300	0.082	0.890	0.009	0.019	145	1.99
275	5550	0.343	0.432	0.075	0.150	692	4.67
275	9180	0.296	0.583	0.040	0.081	616	3.57
275	9200	0.169	0.735	0.032	0.064	494	3.98
275	8170	0.081	0.853	0.022	0.044	296	4.26
305	20600	0.637	0.246	0.029	0.057	895	8.46
305	18200	0.468	0.410	0.034	0.069	1170	6.40
305	20400	0.270	0.627	0.041	0.082	1230	6.88
305	18700	0.169	0.745	0.039	0.078	1330	7.11

Calculations show that the kinetics of reaction (3) on these catalysts are described by the equation

$$w = k \cdot p_{HCl} \cdot p_{(CH_3)_2O}$$ (5)

Figure 3 shows that the experimental data agree rather well with eq.(5). /3059

A comparison of the values of reactions (1) and (3) shows that $k_3 < k_1$.

The constants of the Arrhenius equation have the following values for the catalysts studied:

$$B = 5.5 \cdot 10^3 \quad E = 12900 \text{ kcal/mole} \quad (Al_2O_3),$$
$$B = 2.07 \cdot 10^6 \quad E = 5100 \text{ kcal/mole} \quad (ZnCl_2/Al_2O_3),$$
$$B = 4.26 \cdot 10^6 \quad E = 6600 \text{ kcal/mole} \quad (ZnCl_2/AP-3).$$

As in the case of reaction (1), the apparent activation energy on alumina is appreciably higher than on zinc chloride as catalyst.

A consideration of the kinetic measurements shows zinc chloride to be a considerably more selective catalyst than alumina for the synthesis of methyl chloride.

2. Conclusions

1. The kinetics of dehydration of methanol and the hydrochlorination of dimethyl ether on alumina and zinc chloride catalysts is described by second-order equations.

2. The reaction of formation of methyl chloride from dimethyl ether proceeds through successive-parallel stages, the first of which is the rate-determining step.

3. In the kinetic region, zinc chloride is a more selective catalyst than alumina for the synthesis of methyl chloride.

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